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The Self-Reactions of 1-Methoxycarbonyl-1-methylethyl and Higher Ester Radicals: Combination *vs* Disproportionation and Oligomeric Products from Secondary Reactions

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Abstract

The geminate self-reactions of the title methyl, ethyl and butyl ester radicals (2a–c), formed by decomposition of the corresponding azo precursors (1a–c) in the presence of stable nitroxide radical scavengers, were found on the basis of product analysis to comprise combination and disproportionation in the ratios 56 : 44 (methyl), 58 : 42 (ethyl) and 47 : 53 (butyl). In the absence of radical scavengers, extensive oligomerization is observed. Hydrogenation and degradation were used in conjunction with g.l.c.–m.s. to deduce the identities of the dimeric, trimeric and tetrameric products, which were in most cases subsequently confirmed by isolation and n.m.r. analysis. Of particular interest is the highly regioselective disproportionation of radical (3) to give dimethyl 4-methylpent-1-ene-2,4-dicarboxylate (8), and the further reaction of (8) with (2a) to form branched oligomers (10) and (15).

Introduction

Our continuing interest in the origins and effects of abnormal or defect groups in polymers[1] has, to date, been largely confined to those arising in the initiation step of radical polymerization.[2,3] We have recently turned our attention towards those groups which might arise during the termination step,[4–6] namely, by combination or

[1] Solomon, D. H., *J. Macromol. Sci., Chem.*, 1982, **17**, 337; *Chem. Aust.*, 1982, **49**, 192; *Aust. OCCAA Proc. News*, 1981, **18**, 4.

[2] Rizzardo, E., Serelis, A. K., and Solomon, D. H., *Aust. J. Chem.*, 1982, **35**, 2013, and references therein.

[3] Moad, G., Solomon, D. H., Johns, S. R., and Willing, R. I., *Macromolecules*, 1982, **15**, 1188; Cuthbertson, M. J., Moad, G., Rizzardo, E., and Solomon, D. H., *Polym. Bull.*, 1982, **6**, 647; Moad, G., Rizzardo, E., and Solomon, D. H., *Makromol. Chem., Rapid Commun.*, 1982, **3**, 533; *Aust. J. Chem.*, 1983, **36**, 1573; Cuthbertson, M. J., Rizzardo, E., and Solomon, D. H., *Aust. J. Chem.*, 1983, **36**, 1957; Grant, R. D., Griffiths, P. G., Moad, G., Rizzardo, E., and Solomon, D. H., *Aust. J. Chem.*, 1983, **36**, 2447; Johns, S. R., Rizzardo, E., Solomon, D. H., and Willing, R. I., *Makromol. Chem., Rapid Commun.*, 1983, **4**, 29; Chong, Y. K., Rizzardo, E., and Solomon, D. H., *J. Am. Chem. Soc.*, 1983, **105**, 7761.

[4] Serelis, A. K., and Solomon, D. H., *Polym. Bull.*, 1982, **7**, 39.

[5] Moad, G., Serelis, A. K., Solomon, D. H., and Spurling, T. H., *Polym. Commun.*, 1984, **25**, 240.

[6] Cacioli, P., Moad, G., Rizzardo, E., Serelis, A. K., and Solomon, D. H., *Polym. Bull.*, 1984, **11**, 325.

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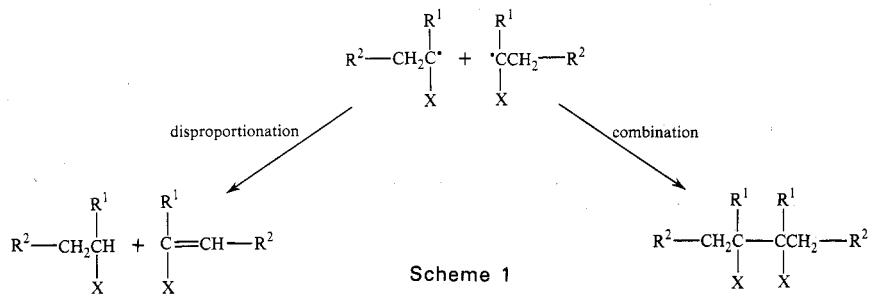
disproportionation between two polymer radicals (Scheme 1). The competition between these two processes has implications not only in the molecular weight distribution of the resulting polymer,[7,8] but also in the different photo-[9] and thermo-lability[6,10,11] and chemical reactivity[12–15] of the substructures thus generated.



Scheme 1

The termination mechanism that prevails for poly(methyl methacrylate) has long been the subject of considerable scrutiny, and debate still continues as to the precise balance between the two possible modes of self-reaction of two poly(methyl methacrylate) radicals.[8,15–19] In keeping with our philosophy that simple model systems are a useful starting point for studying polymerization mechanisms, we chose to approach this problem initially by examining the chemistry of a simple model for

[7] Henrici-Olive, G., and Olive, S., *Makromol. Chem.*, 1963, **68**, 120; Olaj, O. F., Breitenbach, J. W., and Wolf, B., *Monatsh. Chem.*, 1964, **95**, 1646; Hakozaki, J., and Yamada, N., *Kogyu Kagaku Zasshi*, 1967, **70**, 1560 (*Chem. Abstr.*, 1968, **68**, 96263r); Braks, J. G., and Huang, R. Y. M., *J. Appl. Polym. Sci.*, 1978, **22**, 3111.

[8] Braks, J. G., Mayer, G., and Huang, R. Y. M., *J. Appl. Polym. Sci.*, 1980, **25**, 449.

[9] Bevington, J. C., 'Radical Polymerization' p. 138 (Academic Press: (London 1961).

[10] Grassie, N., and Vance, E., *Trans. Faraday Soc.*, 1953, **49**, 184; Grassie, N., and Melville, H. W., *Proc. R. Soc. London, Ser. A*, 1949, **199**, 1, 14, 24, 39; Brockhaus, A., and Jenckel, E., *Makromol. Chem.*, 1956, **18–19**, 262; Malhotra, S. L., Minh, L., and Blanchard, L. P., *J. Macromol. Sci., Chem.*, 1956, **19**, 579.

[11] Geuskens, G., Hellinckx, E., and David, C., *Eur. Polym. J.*, 1971, **7**, 87.

[12] Palit, S. R., and Saha, M. K., *J. Polym. Sci.*, 1962, **58**, 1233.

[13] Saha, M. K., *Indian J. Chem.*, 1964, **2**, 289.

[14] Suen, T. J., and Rossler, D. F., *J. Appl. Polym. Sci.*, 1960, **3**, 126; McNeill, I. C., and Makhdumi, T. M., *Eur. Polym. J.*, 1967, **3**, 637.

[15] Bamford, C. H., and White, E. F. T., *Trans. Faraday Soc.*, 1958, **54**, 268.

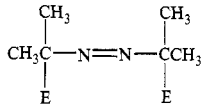
[16] Ayrey, G., and Haynes, A. C., *Eur. Polym. J.*, 1973, **9**, 1029, and references therein.

[17] Bevington, J. C., Melville, H. W., and Taylor, R. P., *J. Polym. Sci.*, 1954, **14**, 463; Schulz, G. V., Henrici-Olive, G., and Olive, S., *Makromol. Chem.*, 1959, **31**, 88; *Z. Phys. Chem.*, 1961, **27**, 1; Bamford, C. H., Dyson, R. W., and Eastmond, G. C., *J. Polym. Sci., Polym. Symp.*, 1967, **16**, 2425; Bamford, C. H., Eastmond, G. C., and Whittle, D., *Polymer*, 1969, **10**, 771; Pramanick, D., Bhattacharyya, R., and Chakraborty, B., *J. Ind. Chem.*, 1984, **12**, 1.

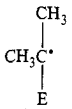
[18] Arnett, L. M., *J. Am. Chem. Soc.*, 1952, **74**, 2027; Arnett, L. M., and Peterson, J. H., *J. Am. Chem. Soc.*, 1952, **74**, 2031; Baysal, B., and Tobolsky, A. V., *J. Polym. Sci.*, 1952, **9**, 171; Hatada, K., Kitayama, T., and Yuki, H., *Makromol. Chem., Rapid Commun.*, 1980, **1**, 51; Pramanick, D., and Chatterjee, A. K., *J. Polym. Sci., Polym. Chem. Ed.*, 1980, **18**, 311, 2585; Jen-Feng, K., and Chuh-Yang, C., *Polym. J.*, 1981, **13**, 453.

[19] Bamford, C. H., Dyson, R. W., and Eastmond, G. C., *Polymer*, 1969, **10**, 885.

poly(methyl methacrylate) radicals, namely 1-methoxycarbonyl-1-methylethyl* (2a), as generated from the diazene precursor (1a). Methyl azoisobutyrate (1a) has been well studied kinetically because of its potential as a polymerization initiator.[20] Product studies have been reported by two groups: Bickel and Waters[21] reported the isolation of a number of monomeric, dimeric and trimeric products from (1a), while Trecker and Foote[22] found the same products by isolation and attempted to quantitate them by gas chromatography. Analogous products were found by Hammond and Fox[23] from decomposition of the ethyl ester (1b). In each case a number of obvious possible oligomeric reaction products were not mentioned, and the quantitative aspects of the self-reaction of (2a,b) were either deficient or ambiguous (see below). In expectation of contributing further to the chemistry of (2), we re-examined the decomposition of (1a) in the presence and absence of various radical scavengers, and also in the presence of added methyl methacrylate. This paper reports our findings on the extent and nature of oligomerization of (2a), and on some quantitative aspects of the self-reaction of (2a) and its higher homologues, the ethyl ester (2b) and n-butyl ester (2c).



(1)



(2)

(a) E = CO_2Me
(b) E = CO_2Et
(c) E = CO_2Bu
(d) E = CN

Results and Discussion

Analysis by g.l.c. of the reaction mixture from decomposition of methyl azoisobutyrate (1a) in chlorobenzene at 80° revealed considerably more products than had been reported by the previous workers[21,22] (Table 1, Scheme 2). Our investigations were confined largely to the tetrameric and lower products (degree of polymerization $n \leqslant 4$) due to expected difficulties in identification of individual higher oligomers. Nevertheless, it was readily apparent that there were more products, namely (10) and (15) (Scheme 3), than could be accounted for on the straightforward but exhaustive basis depicted in Scheme 2. Further decompositions of (1a) were conducted in the presence of added methyl methacrylate (Table 1) to enhance production and facilitate identification of these oligomers.

Methyl isobutyrate, methyl methacrylate and dimethyl tetramethylsuccinate (6a) were identified by comparison with authentic compounds. For the remainder, g.l.c.–m.s. provided a ready distinction between saturated and unsaturated oligomers, the respective molecular weights being $100n+2$ and $100n$. In most cases, the M+1 peak was either weak or absent, and molecular weights were therefore assigned on the

* The most commonly used name for (1a) is 2-carbomethoxyprop-2-yl. This paper, however, will adhere to the IUPAC nomenclature system.

[20] Lewis, F. M., and Matheson, M. S., *J. Am. Chem. Soc.*, 1949, **71**, 747; Mackie, J. S., and Bywater, S., *Can. J. Chem.*, 1957, **35**, 570; Lim, D., *Collect. Czech. Chem. Commun.*, 1968, **33**, 1123; Ziegler, K., Deparade, W., and Meye, W., *Justus Liebigs Ann. Chem.*, 1950, **567**, 141.

[21] Bickel, A. F., and Waters, W. A., *Recl Trav. Chim. Pays-Bas*, 1950, **69**, 312.

[22] Trecker, D. J., and Foote, R. S., *J. Org. Chem.*, 1968, **33**, 3527.

[23] Hammond, G. S., and Fox, J. R., *J. Am. Chem. Soc.*, 1964, **86**, 1918.

Table 1. Products from decomposition of methyl azoisobutyrate in chlorobenzene containing methyl methacrylate at 80°

Methyl azoisobutyrate, 0·10 M. Yields are relative, on a molar basis. Products marked with * or † are diastereomers

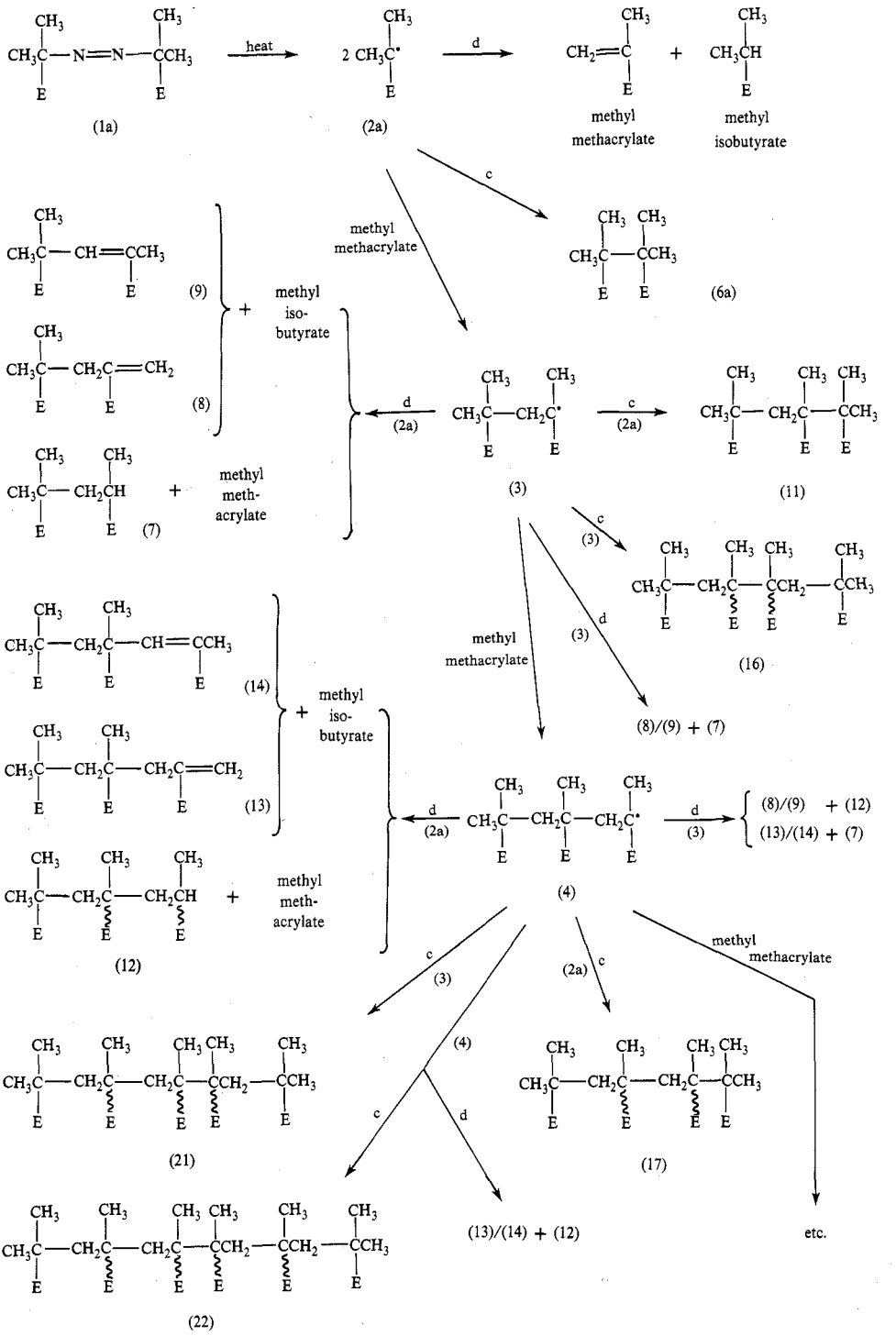
Polymerization (n) and product	Yields (%) at [methyl methacrylate] of 0 M	0·05 M	0·10 M	0·15 M	0·20 M
$n = 1$, [A]	35·3	27·9	23·3	22·9	22·5
[B]	$0·4_5$	$0·7_4$	2·0	2·4	6·8
$n = 2$, (6a)	31·4	22·4	19·2	17·9	14·4
(7)	7·5	10·0	10·2	10·3	11·0
(8)	4·0	7·5	10·8	14·5	16·6
(9)	$0·2_1$	$0·3_1$	$0·3_2$	$0·3_4$	$0·3_3$
$n = 3$, (10)	2·5	4·3	4·2	3·2	1·3
(11)	13·4	12·8	10·4	7·3	3·6
(12)*	$0·1_8$	$0·8_7$	1·3	1·4	1·3
(12)*	$0·5_3$	1·9	2·9	3·4	3·3
(13)	$0·0_9$	$0·2_1$	$0·4_8$	1·0	2·4
(14)	$0·0_3$	$0·1_0$	$0·1_5$	$0·1_7$	$0·1_6$
$n = 4$, (15)	$0·4_5$	$0·6_8$	$0·8_7$	$0·3_4$	$0·0_9$
(16)*	1·3	2·5	2·7	2·4	1·6
(16)*	1·2	2·6	2·8	2·4	1·7
(17)†	$0·3_2$	$0·7_9$	$0·9_2$	$0·8_0$	$0·5_3$
(17)†	$0·7_4$	1·6	2·0	1·7	1·1
(18)	$0·03_2$	$0·6_2$	1·5	2·0	2·3
(19)	—	—	$0·0_5$	$0·1_6$	$0·6_3$
(20)	—	—	$0·0_2$	$0·0_5$	$0·1_2$
$n \geqslant 5$, (21)*	$0·1_5$	$0·9_3$	1·4	1·3	2·1
(21)*	$0·1_1$	$0·6_5$	$0·9_7$	$0·9_1$	1·4
others	$0·0_7$	$0·6_4$	1·9	3·0	5·3

[A] Methyl isobutyrate.
[B] Methyl methacrylate.

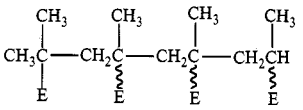
basis of a strong diagnostic M−31 peak.[24] Identities of unsaturated oligomers were confirmed by catalytic hydrogenation of the mixture, which led to disappearance of all peaks which had shown molecular weights of $100n$. In the case of the major unsaturated dimer (8), the terminal nature of the double bond was subsequently established from the n.m.r. spectrum of the isolated compound. The structures of trimer (13) and tetramer (19) then follow by analogy. Double bond positions in the minor unsaturated products, diester (9), triester (14) and tetraester (20), without implying stereochemistry, are therefore most likely penterminal. In addition, the identity of the saturated dimer (7) became apparent from an enhanced g.l.c. peak area on hydrogenation of unsaturated dimer (8), and was subsequently confirmed by the n.m.r. spectrum of the isolated compound.

The two types of saturated products, those derived by combination of two radicals and those derived by disproportionation, were initially distinguished on the basis of changes in relative yields caused by decomposing methyl azoisobutyrate (1a) in the presence of extra methyl methacrylate. For example, trimer (11) is uniquely formed

[24] Silverstein, R. M., Bassler, G. C., and Morrill, T. C., 'Spectrometric Identification of Organic Compounds' 3rd Edn, p. 28 (John Wiley: New York 1974).



Scheme 2. E = CO_2Me; c, combination; d, disproportionation.



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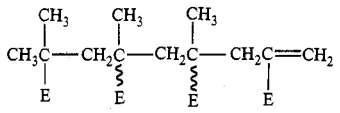

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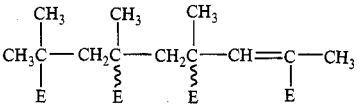
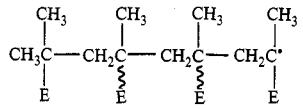
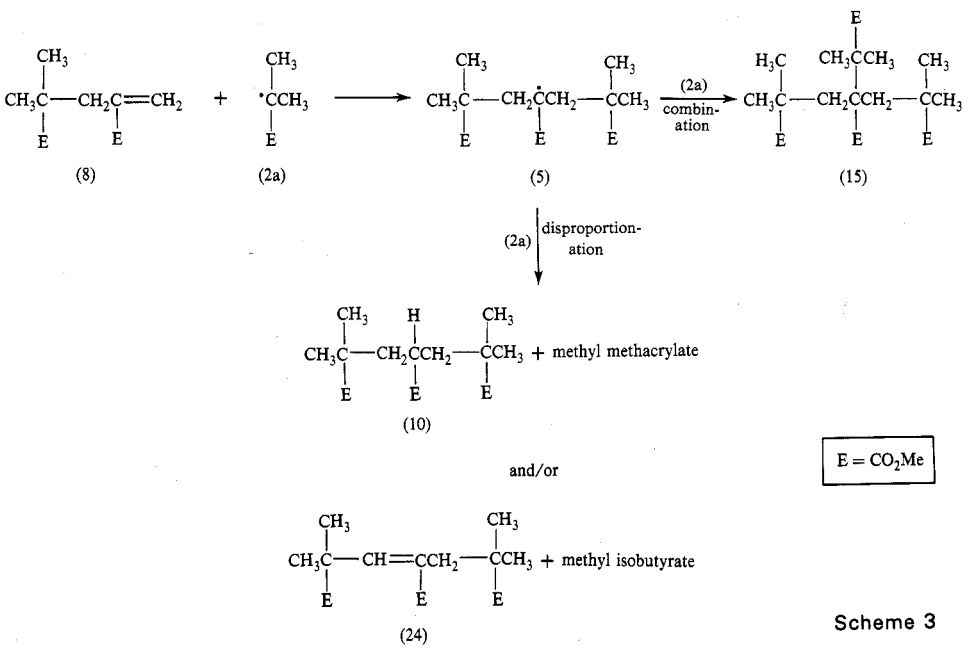


(20)



(23)

by combination of radicals (2a) and (3), whereas trimer (12) arises from a number of disproportionation reactions involving radical (4) in which the latter acts as a hydrogen abstractor (acceptor). As the concentration of added methyl methacrylate is increased, formation of (4) is enhanced at the expense of (2a) and (3), so that the yield of (12) relative to (11) should increase, as is in fact observed. Similarly, the yield of (18), a disproportionation product from radical (23), increases markedly relative to tetraesters (16) and (17), which are combination products of (3)+(3) and (4)+(2a) respectively.



Scheme 3

Further support for these assignments was obtained by chemical degradation, based on the fact that saturated disproportionation products have a C–H bond adjacent to a terminal ester carbonyl, whereas combination products have quaternary carbons adjacent to all ester groups. Thus, after separation into trimer and tetramer fractions by distillation, the trimer mixture was heated with potassium t-butoxide in

tetrahydrofuran, and peak disappearance was monitored by g.l.c. Only one of the three saturated components (10), (11) and (12) of this fraction was unchanged, the other two being degraded completely, and therefore must be (11). Similar treatment of the tetramer fraction resulted in no change in all except one of the saturated components (15), (16), (17) and (18), this being degraded completely, and which therefore must have structure (18). N.m.r. confirmation of structural assignments to (11), (12) and (16) was obtained after isolation.

The presence of an extra saturated disproportionation product (10) of $n = 3$ and an extra combination product (15) of $n = 4$ seemed best accounted for by addition of (2a) to unsaturated diester (8), and the resulting highly hindered radical (5) disproportionating with (2a) to give (10) and methyl methacrylate, or combining with (2a) to give (15) (Scheme 3). That the yield of (8) relative to its saturated counterpart (7) decreases towards low methyl methacrylate concentrations, whereas the ratio of yields of (9) to (7) remains constant, indicates competition between (8) and methyl methacrylate for radical (2a), and is therefore in accord with this proposition. Furthermore, the two products (10) and (15) on isolation exhibited n.m.r. spectra completely in accord with the proposed structures. It should be noted that no unsaturated disproportionation product (24) from radical (5) could be detected, presumably because the steric crowding in the transition state for disproportionation between (5) and (2a) leading to (10) and methyl methacrylate would be less severe than that leading to (24) and methyl isobutyrate.

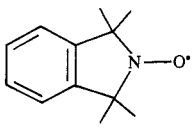
Bickel and Waters[21] reported only the formation of methyl isobutyrate, methyl methacrylate, dimers (6a) and (7) and trimer (11) from methyl azoisobutyrate (1a). Their analysis, however, depended on separation of individual components by fractional distillation. Trecker and Foote reported trimer (12) in addition to the above, but since their analysis seems to be based on g.l.c., it is surprising that a range of products which could rationally be expected to accompany these (Scheme 2 and Table 1) appear not to have been found.[22] A particularly noteworthy absence is that of the unsaturated dimer (8). However, in their examination of the analogous ethyl ester (2b) Hammond and Fox did mention the occurrence of a further 7% of unidentified products.[23]

The terminal position of the double bond in the major unsaturated disproportionation product (8) from (3) is of some significance. The relative yields of (8) and (9) (Table 1) indicate a very high degree of selectivity for hydrogen removal from methyl as opposed to methylene adjacent to the radical centre in (3). Although this sort of selectivity might be expected on steric grounds, there exists little precedent for such an observation. In a recent report of the analogous oligomers from 1-cyano-1-methylethyl (2d) from azoisobutyronitrile (1d) (cf., Scheme 2, E = CN), we indicated that there was only one olefinic product in each *n*-meric fraction.[4] We have subsequently been able to show spectroscopically that these too have terminal unsaturation, at least for $n = 2$ and 3. In this case, however, there was no variation in relative yields and no extra products to indicate that these alkenes were participating in secondary reactions (cf. Scheme 3, E = CN).

Kämmerer *et al.* have recently described the products obtained from the reaction of 4-alkylphenyl methacrylates with 1-cyano-1-methylethyl (2d), which was present in great excess, and under which condition polymerization was suppressed.[25] The

[25] Kämmerer, H., and Pachta, J., *Makromol. Chem.*, 1976, **177**, 3481; Kämmerer, H., Pachta, J., and Ullner, H., *Makromol. Chem.*, 1978, **179**, 1419.

predominant unsaturated disproportionation products were found to have terminal double bonds, and products analogous to (10) were isolated, indicating that these terminal double bonds had undergone addition by (2d) (cf. Scheme 3). One implication of these observations is that unsaturation formed by disproportionation in poly(methyl methacrylate) is most likely terminal, in accord with the usual assumption which has received only indirect experimental support.[11,15] Another possibility which is raised is that terminally unsaturated poly(methyl methacrylate) might be subject to attack by initiating or polymer radicals under polymerization conditions,[15] particularly at high conversion.



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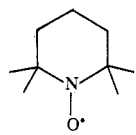

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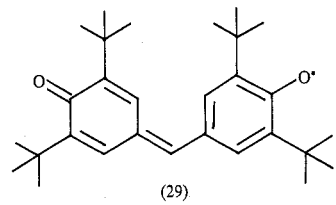

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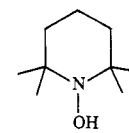


(30)

The proportion of radical pairs which react by combination as opposed to disproportionation (the ratio c/d) can in principle be obtained directly by comparison of the yields of the products from the respective processes. However, in an unrestrained reaction system such as described above, there is room for considerable uncertainty, in that although each combination product defines a unique radical pair, the corresponding disproportionation products can arise from a variety of reactions. For example, although (6a) can only be formed by the self-reaction of (2a), the corresponding disproportionation products from this self-reaction, methyl isobutyrate and methyl methacrylate, can also be derived from the reaction of (2a) with any other radical that might be present (Scheme 2 and beyond; Scheme 3). Furthermore, the unsaturated disproportionation products, e.g. methyl methacrylate from (2a), (8) from (3), etc., are usually consumed, to varying degrees, by secondary reactions. Therefore, in order that the relative yields of (6a) against methyl isobutyrate and/or methyl methacrylate should accurately reflect the relative importance of combination and disproportionation for the self-reaction of (2a), decompositions of methyl azoisobutyrate (1a) were carried out in the presence of suitable concentrations of radical scavengers (Table 2). For this purpose, stable free radicals, namely 1,1,3,3-tetramethylisoindolin-2-yloxyl (27), 2,2,6,6-tetramethylpiperidin-1-yloxyl (28) and galvinoxyl (29) were used rather than even-electron scavengers to avoid possible complications that might arise from formation of new radical species. Under such constraints, only the geminate reaction of radical pairs (2a) from methyl azoisobutyrate (1a) is observed, since all radicals which escape from the solvent cage are scavenged by the added radical traps,* resulting in no propagation-derived products. Nevertheless, some problems do remain, and these are exemplified with

* For detailed discussion of the cage effect, see Lorand and Koenig and Fischer.[26]

[26] Lorand, J. P., in 'Progress in Inorganic Chemistry' (Ed. S. J. Lippard) Vol. 17, Part 2, 'Inorganic Reaction Mechanisms' (Ed. J. O. Edwards) p. 207 (John Wiley: New York 1972); Koenig, T., and Fischer, H., in 'Free Radicals' (Ed. J. K. Kochi) Vol. 1, p. 157 (John Wiley: New York 1973).

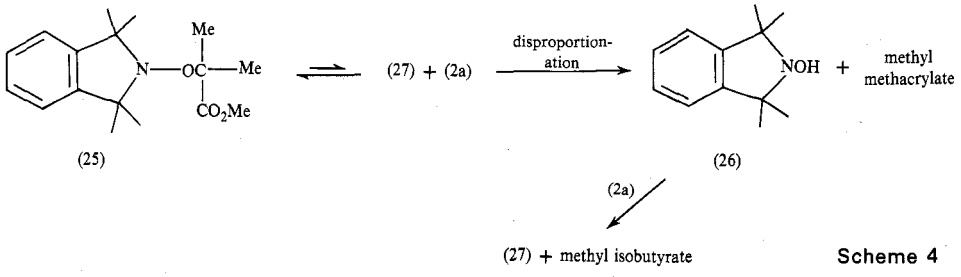
respect to the isoindolinyloxyl adduct (25) (Scheme 4). Firstly, nitroxide-radical adducts such as (25) exhibit facile reversible homolysis at elevated temperatures, and with protracted reaction times, appreciable irreversible hydrogen transfer from (2a) to nitroxide (27) (that is, disproportionation) occurs. The result is a significantly enhanced yield of methyl methacrylate, typically 2–4 fold over methyl isobutyrate, which precludes the use of olefin formation as a measure of c/d. A less severe and more manageable problem appears to be that the hydroxylamine (26) formed in the above disproportionation can act as a hydrogen donor toward (2a) (Scheme 4). This results in slight enhancement in relative yield of methyl isobutyrate, but which can be easily suppressed by increasing the initial concentration of (27), which competes with the hydroxylamine (26) for (2a).

Table 2. Molar ratios of dimethyl tetramethylsuccinate (6a) to methyl isobutyrate from the decomposition of methyl azoisobutyrate (1a) in chlorobenzene containing radical scavengers at 80°

Methyl azoisobutyrate, 0·02 M. Radicals used: 1,1,3,3-tetramethylisoindolin-2-yloxyl (27), 2,2,6,6-tetramethylpiperidin-1-yloxyl (28), galvinoxyl (29)

Radical (27)		Radical (28)		Radical (29)		Methyl methacrylate	
Ratio	Concn (M)	Ratio	Concn (M)	Ratio	Concn (M)	Ratio	Concn (M)
44 : 56[A]	0·03	56 : 44[B]	0·05	40 : 60	0·05	47 : 53	—
55 : 45	0·40	56 : 44	0·05	46 : 54	0·20	45 : 55	0·05
		57 : 43[C]	0·05	50 : 50[D]	0·20	45 : 55	0·10
		55 : 45	0·40			44 : 56	0·15
						37 : 61	0·20

[A] 0·01 M azo ester (1a).
[B] 70° for 72 h.
[C] 90° for 12 h.
[D] 0·005 M azo ester (1a).



Scheme 4

The decreased relative yield of methyl isobutyrate at higher isoindolinyloxyl (27) concentration (Table 2) indicates that reduction of (2a) does occur when (27) is used as a scavenger. On the other hand, the absence of any significant change with increased tetramethylpiperidinyloxyl (28) concentration (Table 2) bespeaks an absence of reduction of (2a) when this nitroxide is used as a radical scavenger. Radical adducts

of both (27) and (28) have been shown to be thermally unstable, and indeed, those of (28) more so than those of (27).[27] Consequently, the difference in production of methyl isobutyrate must arise from the hydrogen donating properties of the respective hydroxylamines (26) and (30).

It has been stated that galvinoxyl (29) reacts with other radicals by coupling rather than by hydrogen abstraction.[28] However, the variation in relative yields observed on varying the galvinoxyl concentration (Table 2) is suggestive of processes akin to those which can occur in nitroxide containing systems (Scheme 4). Furthermore, hydrogalvinoxyl, the product which would eventuate from hydrogen abstraction, constitutes a difficultly removable contaminant of galvinoxyl, and one which would effect reduction of (2a), also leading to enhanced relative yields of methyl isobutyrate (Table 2).

In the absence of scavengers of the stable radical type, the ratio of dimer (6a) to methyl isobutyrate is seen to decrease with added methyl methacrylate (Table 2). As mentioned earlier, methyl isobutyrate can also be derived by disproportionation of (2a) with higher radicals formed by propagation. Addition of methyl methacrylate increases the amount and extent of propagation, and therefore the methyl isobutyrate produced in this way would also be increased, thus accounting for the trend apparent in Table 2.

In view of the foregoing discussion, we believe that the data presented in Table 2 point to a c/d ratio of 56 : 44 for the self-reaction of 1-methoxycarbonyl-1-methylethyl (2a). The telling points are the approximately constant ratio (56 : 44) of dimer (6a) to methyl isobutyrate in the presence of piperidinyloxyl (28), and convergence of this ratio to the same value with increasing isoindolinyloxyl (27) concentration.* It should be noted that since this value (56 : 44) of c/d is measured by taking advantage of the cage effect (24% of the initial radicals generated, on the basis of absolute yields determined by reference to an internal standard) it strictly applies only to the geminate reaction of (2a) with itself. Although there may be some basis for expecting different c/d values for geminate and encounter reactions of radicals,[29] the limited available data indicate that, in the absence of unusual solvent effects (e.g., high viscosity), this appears not to be the case.[29–32]

* Trecker and Foote[22] reported values of c/d in the range 1·61–1·69 for (2a), based on relative yields of (6a) and methyl isobutyrate in a scavenger-free reaction. A similar value (1·81) is implied from product yields in the presence of galvinoxyl (29). The validity of the interpretation of these values, however, should properly be assessed in the light of the problems discussed above. Similarly, their reported slight increase in c/d for (2a) with temperature in the absence of scavengers should be viewed with caution. Comment on the actual numerical differences to our results would be undue since descriptions of analytical procedures are vague. We do note, however, that application of our g.l.c. detector response correction factor to these earlier results largely removes the discrepancies.

[27] Rizzardo, E., and Solomon, D. H., unpublished data.

[28] Bartlett, P. D., and Funahashi, T., *J. Am. Chem. Soc.*, 1962, **84**, 2596.

[29] Gibian, M. C., and Corley, R. C., *Chem. Rev.*, 1973, **73**, 441.

[30] Schuh, H., and Fischer, H., *Int. J. Chem. Kinet.*, 1976, **8**, 341; *Helv. Chim. Acta*, 1978, **61**, 2463.

[31] Tanner, D. D., and Rahimi, P. M., *J. Am. Chem. Soc.*, 1982, **104**, 225; Abuin, E. B., Encinas, M. V., Diaz, S., and Lissi, E. A., *Int. J. Chem. Kinet.*, 1984, **16**, 503.

[32] Serelis, A. K., and Solomon, D. H., unpublished data.

The self-reactions of the ethyl (2b) and butyl (2c) ester radicals, from the corresponding azo esters (1b)[23,33] and (1c),[33,34] were also examined in a similar fashion. In the absence of radical scavengers there were obtained product mixtures which on the basis of g.l.c.–m.s. appeared qualitatively similar to those described for the methyl ester, and which were not investigated further. Decomposition of azo esters (1b) and (1c) in the presence of isoindolinyloxyl (27), piperidinyloxyl (28), or galvinoxyl (29) gave only products derived from the respective geminate reaction of (2b) and (2c). The ratios c/d in each case were determined from the relative yields of the appropriate monomeric and dimeric products—ethyl isobutyrate and diethyl tetramethylsuccinate (6b) from (1b), and butyl isobutyrate and dibutyl tetramethylsuccinate (6c) from (1c) (Table 3). The values shown in Table 3 determined at high relative concentrations of scavenger, at which, for the reasons discussed earlier, the product ratios best reflect the true geminate reaction product ratios. Thus there appears to be a slight increase in combination over disproportionation on changing from methyl to ethyl (c/d ~ 58 : 42), and a significant increase in disproportionation on going to a butyl ester (c/d ~ 47 : 53).

Table 3. Combination to disproportionation ratios for geminate self-reactions (80°) of ester radicals (2a–c)

Solutions were 0·050 M in azo ester and 0·40 M in scavenger. Methyl (1a) and ethyl (1b) azo esters were decomposed in chlorobenzene; butyl (1c) azo ester was decomposed in benzene. The ratio combination/disproportionation is taken as the molar ratio of tetramethylsuccinate (6) to isobutyrate esters

Scavenger	(2a) (Me)	(2b) (Et)	(2c) (Bu)
(27)	55 : 45	58 : 42	45 : 55
(28)	56 : 44	58 : 42	47 : 53
(29)	50 : 50	59 : 41	43 : 57

The termination reactions of polymethacrylate esters have been reported as showing a change of similar magnitude in c/d on varying the ester alkyl group from methyl to butyl.[16,19] In both of these studies, poly(ethyl methacrylate) exhibited an intermediate value of c/d, in one case close to the methyl value,[19] but near the butyl value in the other.[16] Furthermore, Ayrey and Haynes examined a series of poly(alkyl methacrylates) having even larger ester groups and found a further trend towards increased disproportionation with increasing bulk.[16] It would seem reasonable to expect such an effect to arise by combination being retarded more than disproportionation by increased remote steric bulk.

Also worthy of mention is the absence of any significant variation in c/d for (2a) over the temperature range 70–90° (Table 2). This contrasts with reports of sometimes large decreases in c/d with increasing temperature for termination in poly(methyl methacrylate).[17] On the other hand, simple radicals most often exhibit opposite behaviour, namely increasing c/d with increasing temperature.[29,30] The differences are obviously of relevance to the validity of using model systems as probes

[33] Gritsenko, F. R., Spirin, Y. L., Kochetova, G. I., and Kochetov, D. P., *Ukr. Khim. Zh.*, 1977, **43**, 962 (*Chem. Abstr.*, 1977, **87**, 185001p).
[34] Winterle, J. S., and Mill, T., *J. Am. Chem. Soc.*, 1980, **102**, 6336.

for polymerization mechanisms. However, the limited number and structural variety of examples does not, at this stage, permit any reasonable conclusions to be drawn.

Finally, a limited amount of semiquantitative information on other radical–radical reactions can be extracted from our data. Thus, the reaction of radical (5) with (2a) (Scheme 2) has already been mentioned. From the relative product yields (Table 1) it can be seen that the ratio of the combination and disproportionation products (15) and (10) is relatively constant (0·18, 0·17 and 0·20) at low methyl methacrylate concentrations (0–1·0 M), but decreases at higher concentrations. This argues that (5) exhibits some degree of preference for reaction with (2a), most likely for steric reasons, so that formation of (10) through reactions with higher radicals only becomes significant when (2a) is most effectively scavenged by high concentrations of methyl methacrylate. Therefore, a value of about 0·2 (that is, 17 : 83) could be considered a reasonable estimate of c/d for the reaction of (5) with (2a).

Of particular interest from the viewpoint of models for termination in poly(methyl methacrylate) is the self-reaction of the dimeric radical (3). From the relative yields in Table 1, the highest ratio of combination (16) to saturated disproportionation (7) products observed is 0·54, or 35 : 65 ([methyl methacrylate] = 0·10 M). Remembering that c/d values based on relative product yields will usually be deflated because of the multiple origins of the disproportionation products, this ratio must represent the point at which the extraneous contributions to the denominator are least, albeit probably still not zero. Therefore, 0·54 is the lowest possible value of c/d for the self-reaction of (3); that is, the extent of combination which occurs must be greater than 35% and disproportionation must correspondingly be less than 65%.

A similar consideration can be applied to the reaction between radicals (2a) and (3). The ratio of the yield of combination product (11) to the average of the yields of the two possible saturated disproportionation products, methyl isobutyrate and (7), shows a maximum of 0·67 at [methyl methacrylate] = 0·05 M. Therefore the pathway by which radicals (2a) and (3) react must comprise at least 40% combination and, correspondingly, less than 60% disproportionation. Clearly (3) is a more appropriate model for poly(methyl methacrylate) radical than is (2a), and we are currently examining routes to possible direct precursors in order to investigate more fully its chemistry.

The degree of correspondence between the behaviour of macroradicals and their simple models remains to be established, primarily because of the uncertainties inherent in analysis of macromolecular systems. In the particular case of termination in the polymerization of methyl methacrylate, it seems certain that considerable disproportionation does occur, but it is the extent which defies consensus. More qualitative aspects of the chemistry which attends disproportionation in methyl methacrylate polymerization, namely the formation of terminal double bonds and the possibility of their reaction with suitable radicals as suggested by observations described and cited herein, also remain to be verified.

Experimental

Infrared spectra were determined as liquid films or KBr discs (solids) on a Unicam SP100 or a Perkin–Elmer 577 grating spectrometer. N.m.r. spectra were recorded on a Varian EM-390 or a Bruker WM250 spectrometer with (D)chloroform as solvent and tetramethylsilane as an internal standard. Chemical-ionization mass spectra were obtained with a Finnigan 3300 mass spectrometer with methane as a reagent gas. G.l.c.–m.s. determinations were on the same instrument with column A (below) and methane as carrier/reagent gas. Gas–liquid chromatographic (g.l.c.)

analyses were carried out on a Varian Vista 4600 instrument attached to a Varian Vista CDS 401 data system, or on a Perkin–Elmer Sigma 3B attached to a Spectra–Physics SP4270 integrator. Both instruments were fitted with flame ionization detectors. The following columns were used: (A) 3% Dexsil 300 on Chromosorb W/HP (100/120), glass, 2·0 m by 2·0 mm; (B) 10% Silar 10C on Chromosorb W/HP (100/120), glass, 2·0 by 2·0 mm; (C) SCOT Carbowax 20M, 52800 NEFF, glass, 54 m by 0·5 mm; (D) bonded WCOT Carbowax 20M, 25000 NEFF, vitreous silica, 12 m by 0·3 mm. Preparative g.l.c. was performed on a Pye 104 instrument fitted with a flame ionization detector, by using column (E), 10% SE-30 on Chromosorb W (40/60), glass, 9·1 m by 10 mm. Carrier gas (helium) flow rates were 25 ml/min for A and B, 4·0 ml/min for C, 0·5 ml/min for D, and (nitrogen) 80 ml/min for E. Preparative h.p.l.c. was performed by using a combination of a DuPont column compartment, Altex 110A pump, Altex 420 microprocessor controller, and DuPont infrared detector, and by using a Whatman Partisil M9 column (25 cm by 9·4 mm). Melting points were measured on an Electrothermal melting point apparatus, or on a Kofler hot-stage microscope and are uncorrected, as are boiling points. Microanalyses were carried out by the Australian Microanalytical Service, AMDEL, Melbourne.

All organic extracts were dried over anhydrous Na_2SO_4; 3 : 1 (v/v) ether/dichloromethane was used, and petrol refers to light petroleum of b.p. 40–60°. Benzene[4] and methyl methacrylate[2] were purified as described previously. Chlorobenzene was washed with several portions of conc. H_2SO_4, followed by water, saturated $NaHCO_3$, dried (P_2O_5) and distilled. All solvents used for chromatography were redistilled. 1,1,3,3-Tetramethylisoindolin-2-yloxyl (27) was prepared as described elsewhere.[35] 2,2,6,6-Tetramethylpiperidin-1-yloxyl (28) was kindly supplied by Dr E. Rizzardo (prepared according to ref.[36]) and sublimed before use. Crude galvinoxyl (29) was prepared as described by Kharasch and Joshi;[37] rapid recrystallization from degassed acetone, ethanol, ethyl acetate or petrol gave blue needles of varying m.p. within the range 148–152° (lit.[37] 157·5°). Extensive further recrystallizations gave variations within this range, but no increase on it.

Methyl Azoisobutyrate (1a)

Anhydrous HCl was passed through a stirred suspension of powdered azoisobutyronitrile (1d) (16·4 g, 0·10 mol) in methanol (100 ml) cooled in an ice-bath. When *c.* 60 g of HCl had been absorbed, flow was stopped and the reaction was stirred at ambient temperature until there was obtained a clear solution, which was then kept at 5° for 18 h (overnight). The white precipitate was collected, washed with cold methanol and vacuum-dried. The crude bis(amidate hydrochloride) (23·8 g) was added portionwise to stirred, ice-cooled 12% hydrochloric acid (180 ml), and the reaction mixture was allowed to stand at room temperature for 3 h, whereupon the azo diester (1a) crystallized as fine white needles, m.p. 27–28° (15·6 g). Recrystallization from pentane (−15°) gave chunky white prisms (12·3 g, 68%), m.p. 28° (lit.[21] 31–32°).

Ethyl Azoisobutyrate (1b)[22,23]

The bis(amidate hydrochloride) prepared from azoisobutyronitrile (1d), and dry HCl in ethanol in a similar manner to that described above, was hydrolysed with water (0·5 h), then extracted with ether, dried ($MgSO_4$) and evaporated. The crude oil was purified by crystallization from pentane at −80° to give ethyl azoisobutyrate (1b) as a yellow oil. ν_{max} 1740, 1570, 1380, 1365, 1285, 1180, 1150, 1025 cm^{-1}. N.m.r. δ 4·15, q, *J* 7 Hz, 4H; 1·44, s, 12H; 1·22, t, *J* 7 Hz, 6H. *m/e* 259 (12%, M+1), 213 (67), 197 (6), 185 (13), 157 (28), 139 (12), 127 (14), 121 (22), 115 (35), 99 (14), 88 (35), 87 (65), 79 (22), 62 (100).

Butyl Azoisobutyrate (1c)[33,34]

This compound was prepared by treatment of azoisobutyronitrile (1d) with butanol and dry HCl, followed by extractive workup, as described above. Excess butyl alcohol was removed from the crude product by standing a solution in petrol over anhydrous $CaCl_2$. The resulting alcohol-free oil was crystallized from petrol (−80°) to give a pale yellow oil. ν_{max} 1740, 1565,

[35] Griffiths, P. G., Moad, G., Rizzardo, E., and Solomon, D. H., *Aust. J. Chem.*, 1983, **36**, 397.
[36] Rozantzev, E. G., and Neiman, M. B., *Tetrahedron*, 1964, **20**, 131.
[37] Kharasch, M. S., and Joshi, B. S., *J. Org. Chem.*, 1957, **22**, 1435.

1380, 1360, 1280, 1160, 1060, 1020 cm^{-1}. N.m.r. δ 4·10, t, *J* 7 Hz, 4H; 1·53–1·67, m, 4H, CH_2; 1·45, s, 12H; 1·38, sext, *J* 7 Hz, 4H, CH_2CH_3; 0·93, t, *J* 7 Hz, 6H. *m/e* 315 (45%, M+1), 257 (6), 213 (100), 157 (35), 144 (95), 143 (45), 129 (17), 115 (92), 101 (14), 99 (22), 95 (15), 89 (78), 87 (85), 79 (28), 71 (42).

Dimethyl Tetramethylsuccinate (6a)

A solution of azoisobutyronitrile (1d) (33·6 g, 0·20 mol) in benzene (500 ml) was degassed and heated under reflux under an argon atmosphere for 23 h. Removal of the solvent and recrystallization (ethanol) of the residue gave tetramethylsuccinonitrile (6d) (22·4 g, 82%) as long white leaflets, m.p. 166–170° (lit.[38] 167–167·5°). A suspension of tetramethylsuccinonitrile (6d) (13·6 g, 0·10 mol) in ethanol (50 ml) and water (250 ml) containing sodium hydroxide (50 g, 1·25 mol) was stirred and heated under reflux for 5 h. The hot solution was acidified to pH ⩽ 1 with conc. HCl, cooled and extracted with ether/dichloromethane (2×150 ml). The combined extracts were dried and evaporated to give a white mass of tetramethylsuccinimide (13·1 g, 85%), m.p. 182–190°. Large white leaflets, m.p. 190–193° (lit.[38] 187–188°), were obtained by recrystallization from aqueous ethanol. The crude imide (9·3 g, 0·060 mol) was heated under reflux for 4 h in 60% sulfuric acid (60 ml). Steam distillation followed by extraction of the distillate with ether/dichloromethane (2×100 ml), followed by washing of the extracts with saturated $NaHCO_3$,* drying, evaporation and recrystallization of the residue from petrol gave tetramethylsuccinic anhydride (5·1 g, 54%), m.p. 147–149° (lit.[40] 147°). This anhydride (4·68 g, 0·030 mol) was heated under reflux in methanolic sodium methoxide solution (1·0 M, 100 ml) for 1 h. The cooled solution was acidified with conc. HCl and concentrated. The residue was taken up in ether/dichloromethane (150 ml), washed with water (2×50 ml), dried and evaporated. The crude product (4·58 g) was dissolved in dry methanol (100 ml) containing conc. H_2SO_4 (5 ml) and heated under reflux for 100 h. The cooled reaction was evaporated and the residue was dissolved in ether/dichloromethane (100 ml), washed with water (50 ml), sat. $NaHCO_3$ (2×25 ml), dried and evaporated to give dimethyl tetramethylsuccinate (6a) as a yellow oil (3·0 g) which rapidly crystallized. Recrystallization from petrol afforded coarse prisms (3·0 g, 49%), m.p. 30–32° (lit.[40] 32°).

Diethyl Tetramethylsuccinate (6b)

Diester (6b), dist. 100° (Kugelrohr)/1·5 kPa (lit.[41] 119–121°/11 kPa), was prepared by oxidative dimerization of ethyl isobutyrate as described by Petragnani *et al.*[42] A small amount of ethyl α-iodoisobutyrate by-product was removed by treatment of the crude product with zinc powder (10 equiv.) in ethanol (0·5 h), and extractive workup prior to distillation.

Dibutyl Tetramethylsuccinate (6c)

The above method[42] was also used to prepare *dibutyl tetramethylsuccinate* (6c), dist. 100° (Kugelrohr)/0·08 kPa (Found: C, 67·4; H, 10·8. $C_{16}H_{30}O_4$ requires C, 67·1; H, 10·6%). ν_{max} 1730, 1465, 1385, 1260, 1165, 1140, 1120 cm^{-1}. N.m.r. δ 4·05, t, *J* 6·8 Hz, 4H; 1·55–1·72, m, 4H, CH_2; 1·40, sext, *J* 7 Hz, 4H, CH_2CH_3; 1·25, s, 12H; 0·94, t, *J* 7 Hz, 6H. *m/e* 287 (7%, M+1), 212 (14), 213 (100), 185 (15), 157 (38), 144 (8), 129 (9).

Decomposition of Alkyl Azoisobutyrates (1a–c)

Quantitative analyses.—Solutions (typically 10 ml) of the required concentration of azo ester (1a–c) and the appropriate additive (Tables 1–3) were made in chlorobenzene, for (1a,b), or benzene (1c). These solutions were degassed by three freeze–evacuate–thaw cycles, with liquid

* Acidification of the basic washings gave tetramethylsuccinic acid (3·5 g, 38%), m.p. 202–205° (lit.[39] 190–192°).

[38] Bickel, A. F., and Waters, W. A., *Recl Trav. Chim. Pays-Bas*, 1950, **69**, 1490.
[39] Kharasch, M. S., Skell, P. S., and Fisher, P., *J. Am. Chem. Soc.*, 1948, **70**, 1055.
[40] Goldschmidt, S., Leicher, W., and Haas, H., *Justus Liebigs Ann. Chem.*, 1952, **577**, 153.
[41] Hudson, B. E., and Hauser, C. R., *J. Am. Chem. Soc.*, 1941, **63**, 3156.
[42] Brocksom, T. J., Petragnani, N., Rodrigues, R., and La Scala Teixeira, H., *Synthesis*, 1975, 396.

nitrogen as coolant, then sealed under vacuum (1–2 Pa) and placed in a constant temperature bath at 80° for 24 h (except see Table 2). Analysis of the methyl esters by g.l.c. was performed on 3 columns: A (60–380°) gave the overall distribution, while B (90–270°) and C (80–220°) resolved methyl isobutyrate and methyl methacrylate. Additionally, B gave improved resolution of the diastereomers of (12), (16) and (17), and only columns C and D (of a large number examined) successfully resolved dimers (6a) and (7). The ethyl and butyl esters were analysed on columns A (70–340°) and D (50–230°). Detector response factors for methacrylate and isobutyrate esters with respect to the corresponding tetramethylsuccinates (6a–c) and to an internal standard, tetramethylsuccinonitrile (6d), were determined by analysis of mixtures of accurately known composition. Otherwise, detector response factors for those compounds, in the methyl ester series, which were not available in a pure state were approximated by using isolated oligomer fractions (see below).

Chemical reactions.—(i) A small portion (*c.* 100 mg) of the product mixture obtained from decomposition of (1a) in the presence of methyl methacrylate was dissolved in methanol (10 ml) and stirred with PtO_2 (10 mg) under a hydrogen atmosphere at ambient temperature and pressure until hydrogen uptake ceased. The catalyst was removed by filtration through Celite, and the filtrate was analysed by g.l.c. (columns A, C, as above).

(ii) Each of the trimeric ($n = 3$) and tetrameric ($n = 4$) oligomer fractions (below) was treated in the following way: the ester mixture (*c.* 0·2–0·3) mmol) was dissolved in tetrahydrofuran (5 ml), treated with potassium t-butoxide (170 mg, 1·5 mmol) and stirred and heated under reflux in an inert atmosphere. At intervals, 0·1-ml aliquots were withdrawn, quenched with sat. NH_4Cl solution (0·5 ml), and shaken with ether/dichloromethane (*c.* 0·5 ml). The organic layer was then analysed by g.l.c. (column A, as above).

Product isolation.—A solution of methyl azoisobutyrate (1a) (2·30 g, 10 mmol) and methyl methacrylate (1·50 g, 15 mmol) in chlorobenzene (100 ml) was degassed as described above and kept at 80° for 24 h. The solution was concentrated (<40°/2·3 kPa) and the residue was subjected to slow Kugelrohr distillation at 110°/2·3 kPa, with constant monitoring of the distillate by g.l.c. (column A). There was thus collected a fraction (1·6 g) containing only dimers (6), (7), (8), and a trace of (9). Further distillation, initially at 70°/2 Pa, then at 110°/2 Pa and at 150°/2 Pa, gave fractions containing, respectively, only trimers (10)–(14), trimers and tetramer (10)–(18), and only tetramers (15)–(18). Further distillation (>200°/2 Pa) gave no clear-cut *n*-meric fraction.

The dimer mixture (1·6 g) from the above distillation was separated into two fractions by preparative g.l.c. (column E 140°). The fraction of longer retention time (150 mg) was distilled to give, as a colourless oil, dimethyl 4-methylpent-1-ene-2,4-dicarboxylate (8),[43] b.p. 50° (oven)/5 Pa (Found: C, 60·2; H, 8·1. Calc. for $C_{10}H_{16}O_4$: C, 60·0; H, 8·1%). ν_{max} 1730, 1625, 1440, 1290, 1200, 1155, 995, 950 cm^{-1}. N.m.r. δ 6·18, d, *J* 1·4 Hz, 1H, =CH**H**; 5·50, dt, *J* 1·4, 0·9 Hz, 1H, =C**H**H; 3·71, s, CO_2Me; 3·62, s, CO_2Me; 2·61, d, *J* 0·9 Hz, 2H, CH_2; 1·16, s, 6H, CMe_2. *m/e* 201 (4% M+1), 169 (100), 149 (9), 141 (65). The fraction of shorter retention time (450 mg) was subjected to column chromatography (silica, 3 : 7 dichloromethane/petrol). Dimethyl tetramethylsuccinate (6a) (224 mg) was eluted first, followed by a mixture (80 mg), then by pure dimethyl 2-methylpentane-2,4-dicarboxylate (7) (55 mg), which was distilled to give a colourless oil, b.p. 50° (oven)/5 Pa (lit.[44] 81–82°/2·4 kPa) (Found: C, 59·6; H, 8·7. Calc. for $C_{10}H_{16}O_4$: C, 59·4; H, 9·0%). ν_{max} 1740, 1450, 1300, 1255, 1190, 1160, 1140 cm^{-1}. N.m.r. δ 3·62, s, 6H, 2×CO_2Me;* 2·48, ddq, *J* 8·5, 7, 4 Hz, 1H, CH; 2·07, dd, *J* 14, 8·5 Hz, 1H, C**H**H; 1·63, dd, *J* 14, 4 Hz, 1H, CH**H**; 1·18, s, 3H; 1·15, s, 3H; 1·14, d, *J* 7 Hz, 3H. *m/e* 203 (4%, M+1), 171 (100), 143 (50).

The trimer fraction (0·84 g) from the above distillation was separated into three components by preparative g.l.c. (column E, 185°). The first-eluted fraction was redistilled to give *trimethyl 2,6-dimethylheptane-2,4,6-tricarboxylate* (10) of *c.* 91% purity (column A, 60–380°) as a colourless oil (28 mg), b.p. 120° (oven)/4 Pa (Found: C, 59·8; H, 8·7. $C_{15}H_{26}O_6$ requires C, 59·6; H, 8·7%). ν_{max} 1730, 1480, 1440, 1390, 1375, 1300, 1260, 1200, 1140, 980, 910, 830, 765,

* At high resolution, $\Delta\delta = 0{\cdot}002$ ppm.

[43] Lingnau, J., Stickler, M., and Meyerhoff, G., *Eur. Polym. J.*, 1980, **16**, 785.

[44] Lochmann, L., Rodova, M., Petranek, J., and Lim, D., *J. Polym. Sci., Polym. Chem. Ed.*, 1974, **12**, 2295.

730 cm^{-1}. N.m.r. δ 3·62, s, 6H, 2×CO_2Me; 3·59, s, 3H, CO_2Me; 2·46, tt, *J* 9·5, 3·3 Hz, 1H, CH; 2·06, dd, *J* 14, 9·5 Hz, 2H, CHHCHCHH; 1·60, dd, *J* 14, 3·3 Hz, 2H, CHHCHCHH; 1·16, s, 6H, 2×Me; 1·13, s, 6H, 2×Me. *m/e* 272 (15%), 271 (100, M−31), 269 (11), 244 (6), 243 (42), 211 (29), 201 (5), 102 (5). The second-eluted trimer peak gave, after distillation, trimethyl 2,3,5-trimethylhexane-2,3,5-tricarboxylate (11) of *c.* 97% purity (column A, as above) as a colourless oil (84 mg), b.p. 120° (oven)/4 Pa (lit.[22] 104°/2·4 Pa). Spectral details for (11) agreed in essence with those previously reported.[22] the last eluted fraction was distilled to give, as a colourless oil, trimethyl 2,4-dimethylheptane-2,4,6-tricarboxylate (12)[44] as a 2 : 1 mixture of diastereomers of *c.* 86% purity as a colourless oil (34 mg), b.p. 120° (oven)/4 Pa (Found: C, 59·9; H, 9·1. Calc. for $C_{15}H_{26}O_6$: C, 59·6; H, 8·7%). ν_{max} 1740, 1450, 1385, 1190, 1145, 985, 760 cm^{-1}. N.m.r. δ 3·59–3·66, 6×s, 9H, 6×CO_2Me; 2·41–2·67, m, 0·7H, CH; 2·35–2·47, m, 0·3H, CH; 2·19–2·29, dd, *J* 14, 8·5 Hz, 0·7H, CHHCH; 1·96–2·16, m, 2·3H, CH_2; 1·59–1·66, dd, *J* 14, 3·5 Hz, 0·3H, CHHCH; 1·34, dd, *J* 14, 3 Hz, CH_2CH; 1·01–1·26, complex, 12H, 6×CMe and 2×CHMe.

The tetramer fraction (0·72 g) from the distillation deposited large well formed glassy blocks on standing. These were removed with forceps and rinsed with a little methanol. Recrystallization from methanol afforded coarse prisms of a single diastereomer of *tetramethyl 2,4,5,7-tetramethyloctane-2,4,5,7-tetracarboxylate* (16), m.p. 126·5–127·5° (Found: C, 59·7; H, 8·9. $C_{20}H_{34}O_8$ requires C, 59·7; H, 8·5%). ν_{max} 1730, 1720, 1480, 1460, 1390, 1365, 1230, 1205, 1135, 1065, 980, 825, 765 cm^{-1}. N.m.r. δ 3·63, s, 6H, 2×CO_2Me; 3·61, s, 6H, 2×CO_2Me; 2·27, d, *J* 14·5 Hz, 2H, 2×CHH; 2·21, d, *J* 14·5 Hz, 2H, 2×CHH; 1·19, s, 6H, 2×Me; 1·02, s, 12H, 4×Me. *m/e* 403 (3%, M+1), 401 (4), 372 (20), 371 (100), 343 (11), 311 (5), 202 (8), 201 (12), 102 (9), 101 (10). The remainder of the tetramer fraction was combined with the preceding intermediate fraction (containing $n = 3+4$) and chromatographed on silica (200 g). Elution (0–3% ether/dichloromethane) was monitored by g.l.c. (column A, above). Most fractions comprised mixtures of trimers or tetramers. However, there was obtained a further sample of triester (11) (16 mg) of *c.* 95% purity, and a mixture of the two diastereomers of tetraester (16) (60 : 40) (66 mg). Subtraction of the n.m.r. spectrum of the minor diastereomer (above) from that of the mixture gave the following for the major isomer of (16): δ 3·63, s, 6H, 2×CO_2Me; 3·61, s, 6H, 2×CO_2Me; 2·72, d, *J* 14 Hz, 2H, 2×CHH; 2·03, d, *J* 14 Hz, 2H, 2×CHH; 1·21, s, 6H, 2×Me; 1·02, s, 6H, 2×Me; 0·94, s, 6H, 2×Me. Fractions containing tetraester (15) were combined and further separation was carried out by h.p.l.c. (10% ether/dichloromethane). After three cycles, the main fraction (20 mg, *c.* 80% purity by g.l.c.–column A, as above) had spectral properties consistent with the assigned structure, trimethyl 2,6-dimethyl-4-(1-methoxycarbonyl-1-methylethyl)heptane-2,4,6-tricarboxylate (15).* ν_{max} 1740, 1460, 1390, 1265, 1200, 1145, 1090, 890 cm^{-1}. N.m.r. δ 3·66, s, 6H, 2×CO_2Me; 3·60 and 3·59, 2×s, 6H, 2×CO_2Me; 2·30, d, *J* 15 Hz, 2H, 2×CHH; 1·90, d, *J* 15 Hz, 2H, 2×CHH; 1·34, s, 6H, 2×Me; 1·16, s, 6H, 2×Me; 1·13, s, 6H, 2×Me. *m/e* 372 (20%), 371 (100, M−31), 343 (12), 311 (6), 202 (6), 201 (10), 102 (9), 101 (11). In addition, there were obtained two fractions which contained predominantly diastereomeric mixtures of tetramethyl 2,4,6-trimethylnonane-2,4,6,8-tetracarboxylate (18) [n.m.r. δ 3·6, complex, 12H, 4×CO_2Me; 2·35–2·65, m, 1H, CH; 1·35–2·35, m, 6H, 3×CH_2; 0·9–1·2, 15H, 5×Me. *m/e* 371 (100%, M−31), 343 (18), 311 (8), 202 (5), 188 (5), 102 (10)] and tetramethyl 2,3,5,7-tetramethyloctane-2,3,5,7-tetracarboxylate (17) [n.m.r. δ 3·6–3·7, 12H, 4×CO_2Me; 1·5–2·6, m, 4H, 2×CH_2; 0·9–1·3, 18H, 6×Me. *m/e* 371 (100%, M−31), 344 (10), 343 (20), 103 (11), 102 (6)] respectively.

Nitroxide adducts.—A solution of methyl azoisobutyrate (1a) (1·23 g, 5·3 mmol) and tetramethylisoindolinyloxyl (27) (2·40 g, 12·0 mmol) in benzene was degassed as described above and kept at 80° for 24 h. The solution was then concentrated and the residue was chromatographed on silica (100 g). Elution with 1 : 1 dichloromethane/petrol and monitoring by t.l.c. gave pure adduct (25) (530 mg, 17%). Two recrystallizations from hexane (room temperature to 15°) afforded *methyl 2-methyl-2-(1,1,3,3-tetramethyl-2,3-dihydro-1H-isoindolin-2-yloxy)propionate* (25) as colourless prisms, m.p. 43° (Found: C, 70·3; H, 8·3; N, 5·2. $C_{17}H_{25}NO_3$ requires C, 70·1; H, 8·7; N, 4·8%). ν_{max} 1740, 1460, 1380, 1368, 1325, 1270, 1195, 1170, 1140, 1110, 1015, 990, 925, 875, 820, 760 cm^{-1}. N.m.r. δ 6·95–7·25, m, 4H, ArH; 3·73, s, 3H, CO_2Me; 1·52, s, 6H, CMe_2CO_2Me; 1·39, s, 6H, 2×ring Me; 1·37, s, 6H, 2×ring Me.

* Satisfactory elemental analysis could not be obtained for this compound.

m/e 292 (20%, M+1), 190 (33), 174 (40), 160 (13), 147 (12), 119 (44), 117 (10), 115 (100), 114 (11), 102 (14), 101 (10), 86 (9), 85 (9), 75 (11), 74 (80), 72 (24). In a similar experiment conducted with (28) instead of (27), none of the analogous tetramethylpiperidinyloxyl adduct could be isolated.*

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* Thermal instability of these alkoxyamines (see Discussion) is the presumed reason for the absence of this compound and for the lower than theoretical (~ 70% based on measured cage effect) yield of (23). This piperidinyloxyl adduct has, however, been subsequently isolated[45] by conducting the decomposition at 60°.

[45] Cacioli, P., CSIRO, personal communication.